Glycerol as a cheap, safe and sustainable solvent for the catalytic and regioselective β,β-diarylation of alkenes over palladium nanoparticles

Mathieu Delample, [a,b] Nicolas Villandier,[a] Jean-Paul Douliez,[b] Séverine Camy,[c] Jean-Stéphane Condoret,[c] Yannick Pouilloux,[a] Joël Barrault[a] and François Jérôme*[a]

** Corresponding author: francois.jerome@univ-poitiers.fr*

Supporting information

1) Chemicals: Triethylamine, palladium acetate (II), 3-iodo-4-methylaniline and 3-iodo-4-nitrotoluene were purchased to Sigma-Aldrich. Iodobenzene, n-butyl acrylate, cyclohexyl acrylate, iodonaphtalene and 2,4-dimethoxy-1-iodobenzene were bought to Acros. Glycerol was kindly provided by Stearinerie Dubois Fils. All solvents were purchased to Carlo-Erba and were used without any further purification. The synthesis and characterization of the aminopolysaccharide (AP) has been described in a previous paper (reference 8b in the manuscript).

2) Apparatus: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 DPX 400. Chemical shift are expressed in ppm relative to Me_4Si. IR spectra were recorded on a FT-IR Perkin Elmer (spectrum one) using ATR technology. Mass spectrometry analyses were performed on a GC/MS Varian 1200 Triple quadripole equipped with a column Factor Four VF5MS (30m x 0.25mm x 0.25 mm).

3) Chromatographic analyses

The reaction progress was monitored on a Varian 3300 GPC equipped with a BPX5 column (12m x 0.22 mm; phase thickness: 0.25 μm) supplied by SGE, a Flame Detector Ionization and an injector on-column.

4) Recycling experiments

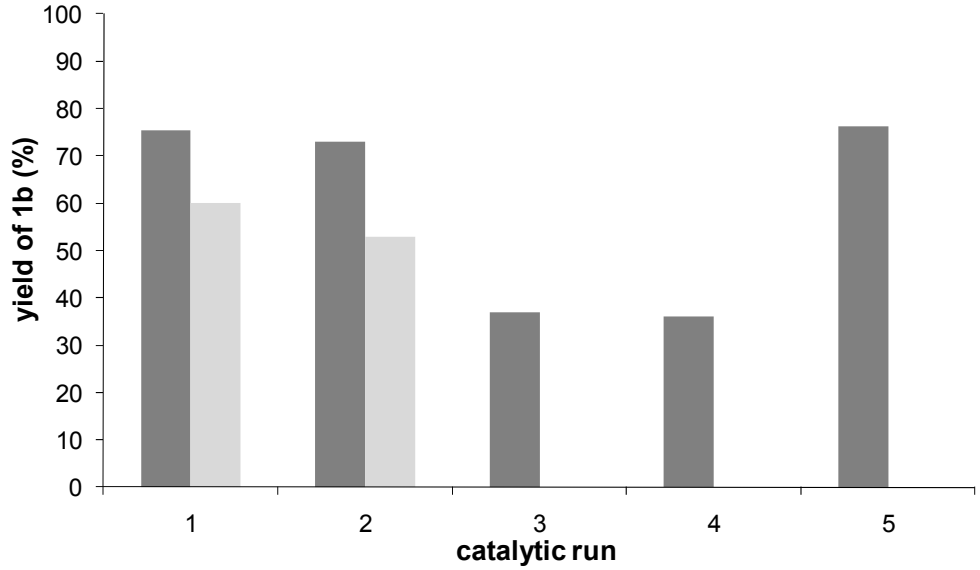


Figure S1 : recycling experiments ▮ GC yield, ▮ after extraction with $scCO_2$

After extraction with $scCO_2$, the Pd/AP catalyst can be selectively extracted from glycerol by liquid-liquid phase extraction. Among all tested organic solvent, dichloromethane was found the best organic solvent allowing a complete and selective extraction of the Pd/AP catalyst from the glycerol mixture. The recovered Pd/AP catalyst has been successfully reused in fresh glycerol without any obvious loss of activity (run 5) confirming that the drop of activity observed cycle after cycle is due to the accumulation of salts in the glycerol phase and not to a catalyst deactivation. Note also that, like in the case of water, triethylamine can be regenerated in glycerol using Amberlyst 21 as anion exchange resin (removal of HI). Therefore, in these experiments, it was possible to fully recycle the Pd/AP catalyst, the glycerol phase and the triethylamine. Conscious that utilization of dichloromethane increases here the environmental impact of our process, we are now working on the design of glycerol-tolerant palladium-based solid catalysts and this aspect, under investigation in our group, will be report in due course in a more specialized journal.

5) Solubility of glycerol in $scCO_2$

The solubility of glycerol into CO_2 under high pressure has been estimated thanks to the equation of Chrastil[1] which correlates the solubility of solids and liquids in supercritical gases with the densities of the gas. Solubility is thus given by the equation (a) where *c* is the concentration of solute in kg per m^3 of a gas, ρ is the density of the gas in $kg.m^{-3}$, *e*, *a* and *b* are solubility parameters. For solubility of glycerol, we used the Adachi and Lu[2] modification who proposed a correlation for parameter *e* (equation b)

(eq. a) $c=\rho^{e}.\exp(a/T+b)$

(eq. b) $e=e_0+e_1.\rho+e_2.\rho^2$

Parameters *e0*, *e1*, *e2, a* and *b* for glycerol have been taken from the works of Sovova *et al.*[3], where they have been fitted from experimental data. Density of carbon dioxide has been calculated thanks to the Lee-Kesler-Plocker (LKP) equation of state that gives a very satisfying representation of the experimental volumetric behaviour of supercritical CO_2.[4] Solubility of glycerol has been calculated at 25 Mbar and 323.15K. Parameters for Chrastil equation, CO_2 density from LKP equation of state and values of solubility are presented in Table 3. Note that similar calculation has been done from water in order to compare its solubility into $scCO_2$ with that of glycerol (parameters *e*, *a* and *b* for water have been taken from the equation of Chrastil[1])

Table S1: solubility of glycerol and water in $scCO_2$ at 25MBar and 323.15K

compound	ρ_{CO2} ($kg.m^{-3}$)	a (K)	b	e	c ($kg.m^{-3}$ of CO_2)
glycerol	837.07	-1672	-13.22	2.3162	0.0604
water	837.07	-2826.4	-0.807	1.549	2.389

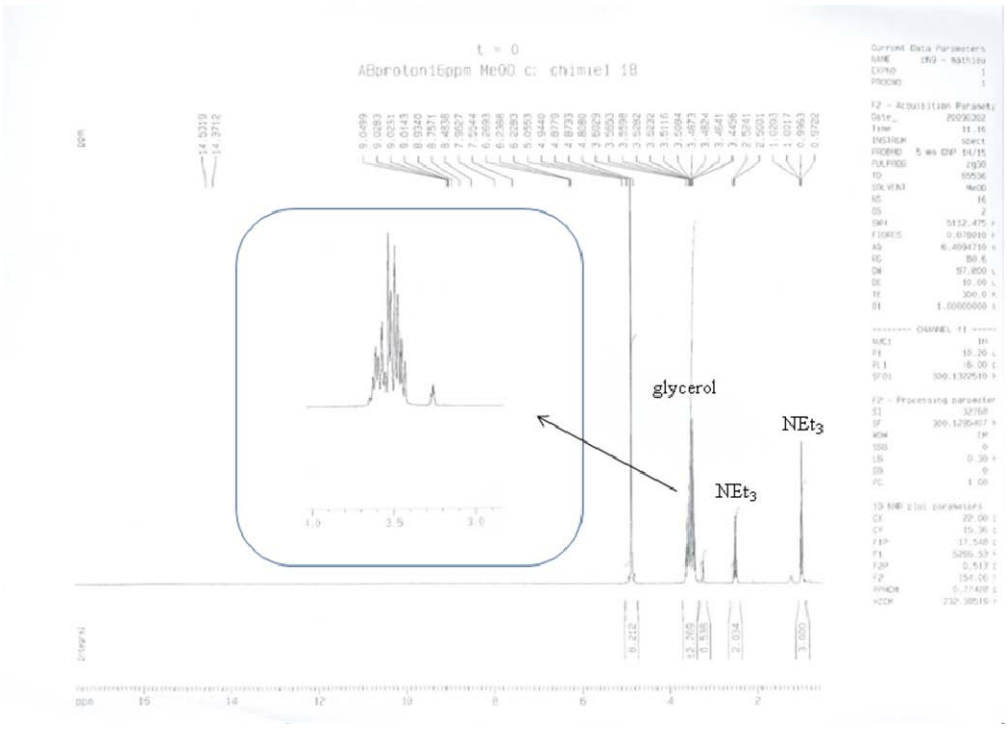
[1] J. Chrastil, *J. Phys. Chem.*, **1982**, 86 (15), 3016-3021

[2] Y. Adachi, B. C.-Y. Lu, *Fluid Phase Equilib.*, **1983**, 14, 147-153

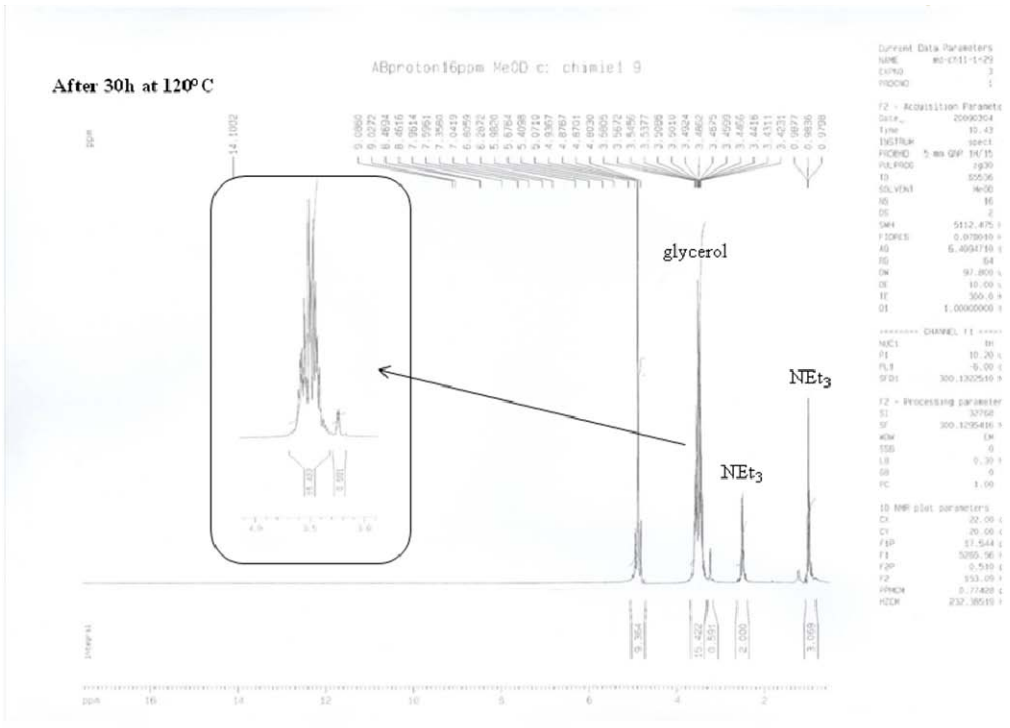
[3] H. Sovova, J. Jez, M. Khachaturyan, *Fluid Phase Equilibria*, **1997**, *137* (1-2), 185-191

[4] U. Plocker, H. Knapp, J. Prausnitz, *Ind. Eng. Chem. Process Des. Dev.*, **1978**, *17*, 324-332

6) Additional schemes, figures and tables



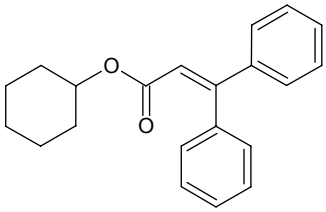
Scheme S1 : ^{1}H NMR spectrum of fresh glycerol with triethylamine and 200mg of Pd/AP



Scheme S2 : ^{1}H NMR spectrum of glycerol with triethylamine and 200mg of Pd/AP after 30 hours of heating at 120°C.

Figure S2 : picture of the SEPAREX SF200 pilot used for $scCO_2$ extractions

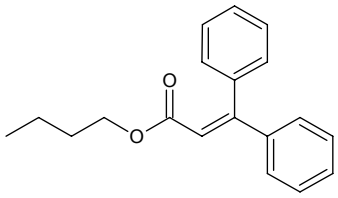
5) Full characterization of the reaction products



1a: *Cyclohexyl 3,3-diphenylacrylate*

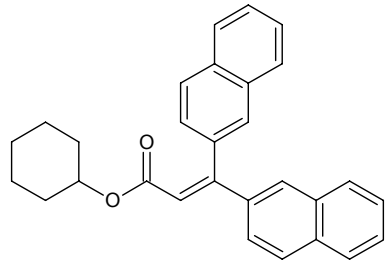
^{1}H NMR (300 MHz, $CDCl_3$): 1.18-1.29 (m, 6H, -CH_2), 1.46 (m, 2H, -CH_2), 1.73 (m, 2H, -CH_2), 4.70 (m, 1H, -CH-O), 6.36 (s, 1H, -CH=), 7.19-7.38 (m, 10H, Ph); ^{13}C NMR (300 MHz, $CDCl_3$) : 23.7, 25.4, 31.5, 72.5, 118.2, 127.9, 128.3, 129.1, 139.2, 140.9, 155.8, 165.7; IR (cm^{-1}) : 2933-2857 (C-H), 1715 (C=O), 1615 (C=C), 1445, 1359, 1259, 1162 (C-O), 1122, 1038, 1016, 1001, 914, 871, 768, 695; MS (EI): m/z = 306 [M^+].

1b: *Butyl 3,3-diphenylacrylate*



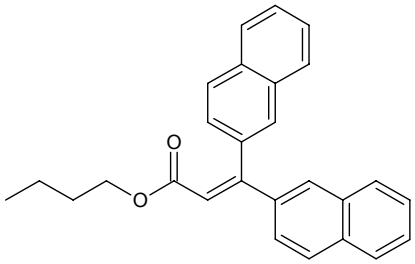
^{1}H NMR (300 MHz, $CDCl_3$): 0.85 (t, *J*=8 Hz, 3H, -CH_3), 1.23 (m, 2H, -CH_2), 1.44 (m, 2H, -CH_2), 3.99 (t, *J*=8Hz, 2H, -CH_2), 6.37 (s, 1H, -CH=), 7.21-7.38 (m, 10H, Ph); ^{13}C NMR (300 MHz, $CDCl_3$) : 15.3, 16.8, 32.9, 64.5, 118.8, 120.9, 129.2-132.8, 141.3, 143.1, 158.7, 168.6; IR (cm^{-1}): 2958-2872 (C-H), 1721 (C=O), 1615 (C=C), 1575, 1491, 1445, 1355, 1262, 1149 (C-O), 1062, 1031, 1001, 873, 769, 695; MS (EI): m/z = 280 [M^+].

1c: *Cyclohexyl 3,3-di-2-naphtylacrylate*



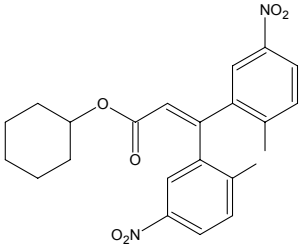
^{1}H NMR (400 MHz, $CDCl_3$): 0.78-1.45 (m, 10H), 4.45 (m, 1H, CH-O), 6.48 (s, 1H, -CH=), 7.23-7.45 (m, 8H, -CH=), 7.69-7.81 (m, 4H, -CH), 7.99 (d, *J*=8 Hz, 1H, -CH), 8.38 (d, *J*=8 Hz, 1H, -CH=); ^{13}C NMR (400 MHz, $CDCl_3$) : 22.5, 24.2, 30.1, 71.6, 124.0-127.7, 129.8, 130.6, 132.7, 133.2, 137.9, 138.7, 150.9, 164.5; IR (cm^{-1}) : 3045-2933-2856 (C-H), 1698 (C=O), 1610 (C=C), 1589, 1507, 1448, 1348, 1319, 1257, 1186, 1162 (C-O), 1122, 1097, 1037, 1016, 981, 908, 890, 864, 801, 772, 736; MS (EI): m/z =406 [M^+].

1d: *Butyl 3,3-di-2-naphtylacrylate*



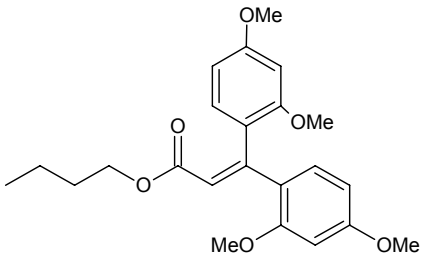
^{1}H NMR (400 MHz, $CDCl_3$): 0.60 (t, *J*=8Hz, 3H, -CH_3), 0.81 (m, 2H, -CH_2), 1.03 (m, 2H, CH_2), 3.74 (t, 2H, -CH_2), 6.49 (s, 1H, -CH=), 7.23 (m, 8H, -CH=), 7.73 (m, 4H, -CH=), 7.95 (d, *J*=8Hz, 1H), 8.37 (d, *J*=8Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): 13.6, 18.9, 30.2, 64.2, 125.1-129.0, 130.8, 131.5, 133.7, 134.2, 138.6, 139.6, 152.5, 166.0; IR (cm^{-1}): 3056-2957-2929 (C-H), 1700 (C=O), 1609 (C=C), 1507, 1462, 1347, 1275, 1185, 1157 (C-O), 1098, 1060, 1021, 865, 803, 772, 736; MS (EI): m/z = 380 [M^+].

1e: *Cyclohexyl 3,3-bis(2-methyl-5-nitrophenyl)acrylate*



IR (cm^{-1}): 2935-2858 (C-H), 1709 (C=O), 1607 (C=C), 1583, 1516-1339 (N=O), 1288, 1225, 1175 (C-O), 1037, 1014, 973, 830, 803, 754 ; MS (EI): m/z = 364 [M^+].

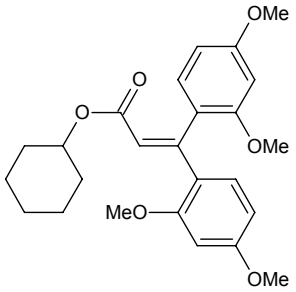
1f: *Butyl 3,3-bis(2,4-dimethoxyphenyl)acrylate*



^{1}H NMR (400 MHz, $CDCl_3$): 0.78 (t, *J*=8 Hz, 3H, -CH_3), 1.17 (m, 2H, -CH_2), 1.39 (m, 2H, -CH_2), 3.62 (s, 3H, -CH_3), 3.64 (s, 3H, -CH_3), 3.71 (s, 3H, -CH_3), 3.73 (s, 3H, -CH_3), 3.90 (t, *J*=8Hz, 2H, -CH_2), 6.29 (m, 1H, -CH=), 6.39 (m, 3H, -CH=), 6.40 (s, 1H, -CH=), 6.84 (m,

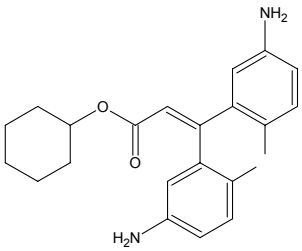
2H, -CH=); ^{13}C NMR (400 MHz, $CDCl_3$) : 13.1, 18.1, 29.3, 54.6, 62.7, 97.7, 103.0, 119.4, 121.7, 122.5, 129.5, 131.0, 147.8, 156.8, 157.9, 159.6, 160.2, 166.0 ; IR (cm^{-1}): 2957-2837 (C-H), 1715 (C=O), 1602 (C=C), 1575, 1503, 1455, 1415, 1353, 1301, 1259, 1206, 1155 (C-O), 1029, 936, 830, 799, 737; MS (EI): m/z =400 [M^+].

1g: *Cyclohexyl 3,3-bis(2,4-dimethoxyphenyl)acrylate*



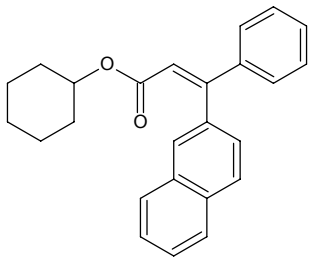
^{1}H NMR (400 MHz, $CDCl_3$): 0.78-1.70 (m, 10H, -CH_2), 3.63 (s, 3H, -CH_3), 3.65 (s, 3H, -CH_3), 3.72 (s, 3H, -CH_3), 3.74 (s, 3H, -CH_3), 4.60 (m, 1H, -CH-O), 6.30 (m, 1H, -CH=), 6.36 (m, 3H, -CH=), 6.40 (s, 1H, -CH=), 6.89 (m, 2H, -CH=); ^{13}C NMR (400 MHz, $CDCl_3$): 21.7, 23.3, 27.9, 29.5, 53.3, 69.8, 96.4, 102.0, 119.1, 120.3, 128.1, 129.3, 146.0, 155.7, 158.5, 164.0; IR (cm^{-1}): 2929-2855 (C-H), 1709 (C=O), 1603 (C=C), 1503, 1453, 1415, 1356, 1301, 1258, 1206, 1155 (C-O), 1031, 936, 831, 798; MS (EI) : m/z =426 [M^+].

1h: *Cyclohexyl 3,3-bis(2-methyl-5-aminophenyl)acrylate*



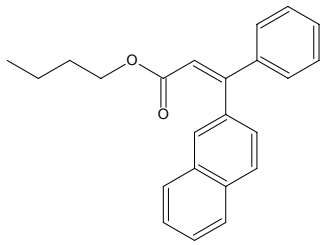
IR (cm^{-1}): 3380 (N-H), 2933-2857 (C-H), 1705 (C=O), 1630 (C=C), 1501, 1449, 1258, 1169 (C-O), 1122, 1037, 1015, 980, 857, 808, 688; MS (EI): m/z =364 [M^+].

2a: *Cyclohexyl (2Z)-3-(2-naphtyl)-3-phenylacrylate*

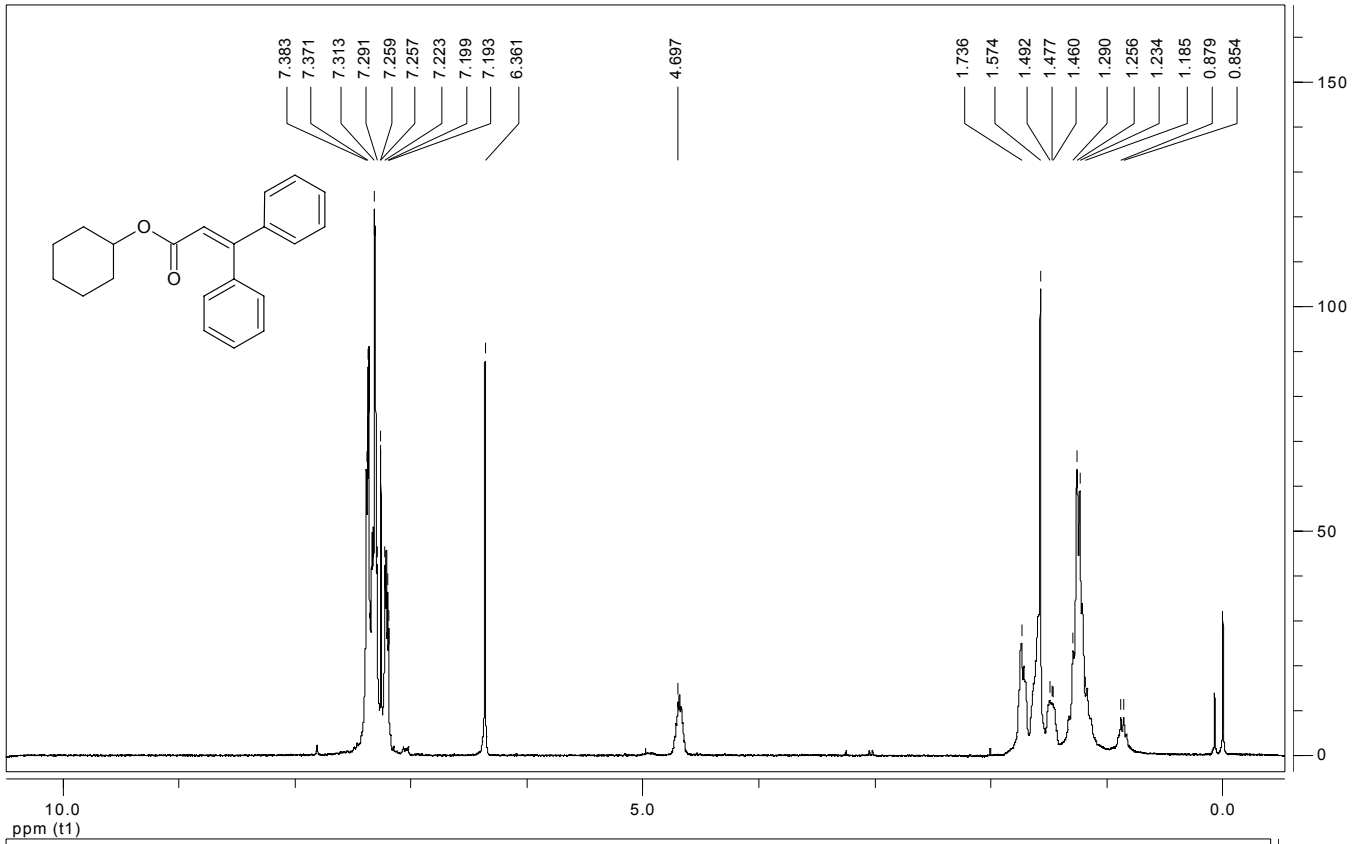


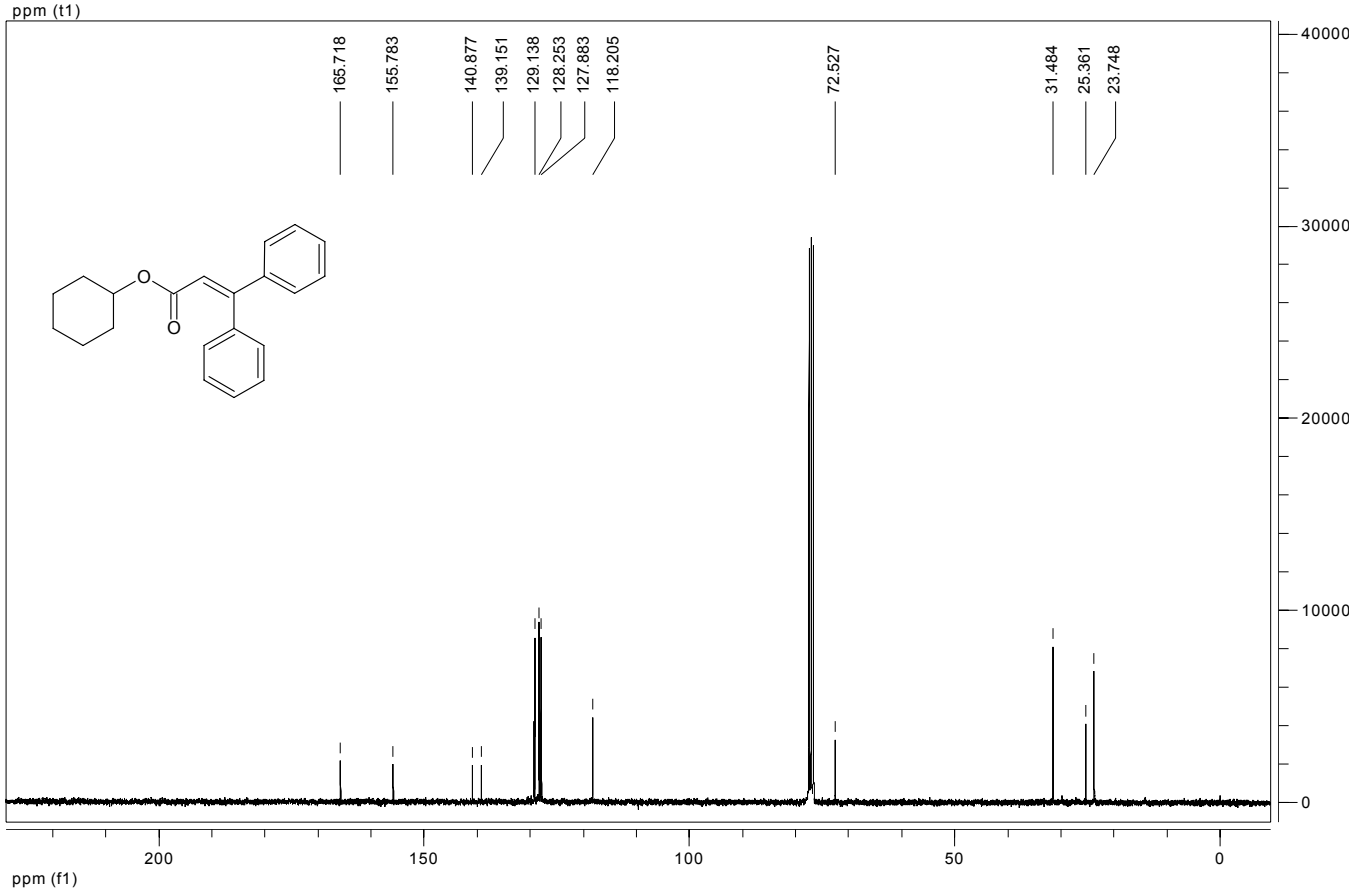
^{1}H NMR ($CDCl_3$, 300 MHz, mixture of cis and trans 50/50): 0.81-1.82 (m, 20H, -CH_2), 4.49 (m, 2H, -CH-O), 4.81 (m, 2H, -CH-O), 6.19 (s, 1H, -CH=), 6.72 (s, 1H, -CH=), 7.25-7.95 (m, 24H); ^{13}C NMR ($CDCl_3$, 300 MHz): 22.6, 24.2, 25.7, 32.0, 73.7, 74.2, 119.5, 121.7, 123.7-140.4, 154.2, 155.0, 165.8, 166.3; IR (cm^{-1}) : 3056-2934-2857 (C-H), 1714 (C=O), 1613 (C=C), 1492, 1446, 1351, 1255, 1163 (C-O), 1122, 1038, 1014, 985, 863, 798, 770, 695; MS (EI): m/z = 356 [M^+].

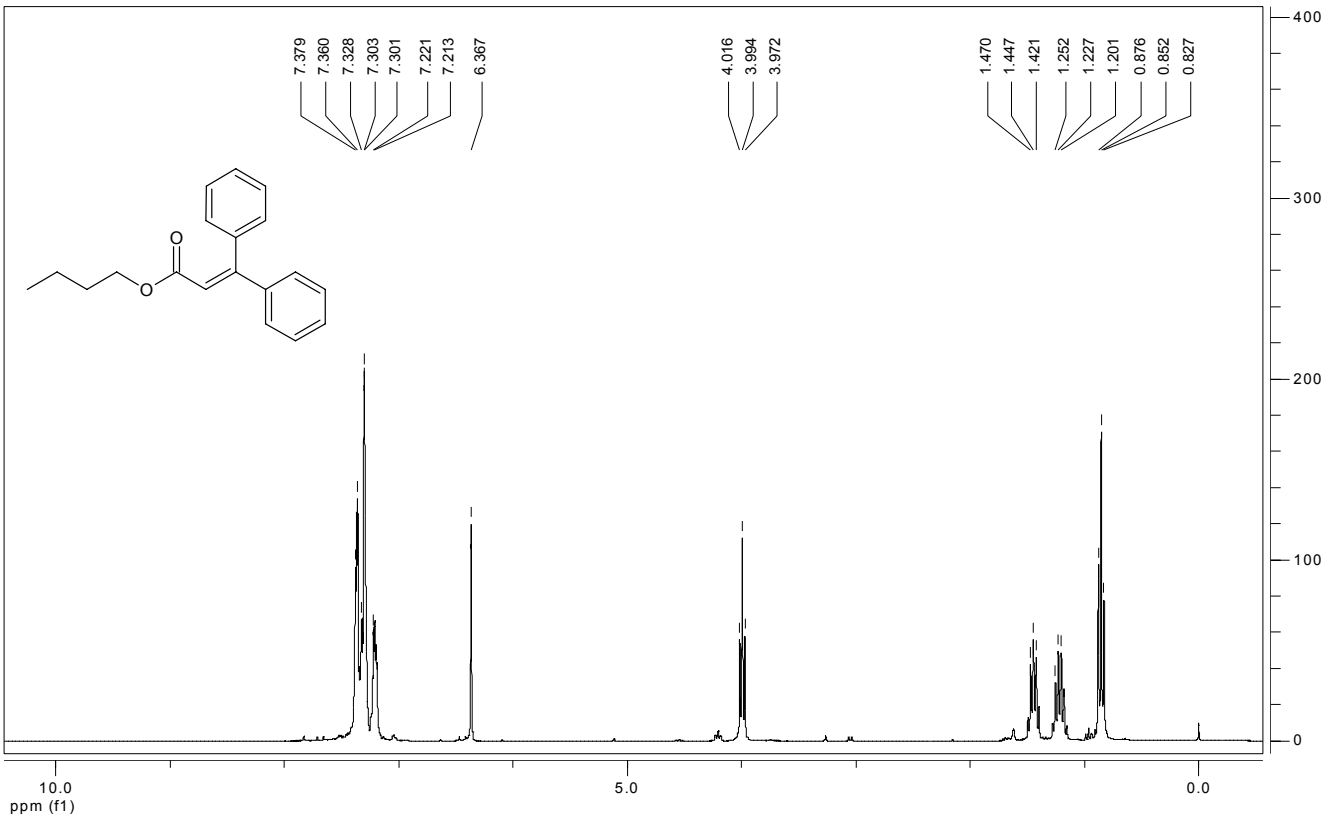
2b: *Butyl (2Z)-3-(2-naphtyl)-3-phenylacrylate*

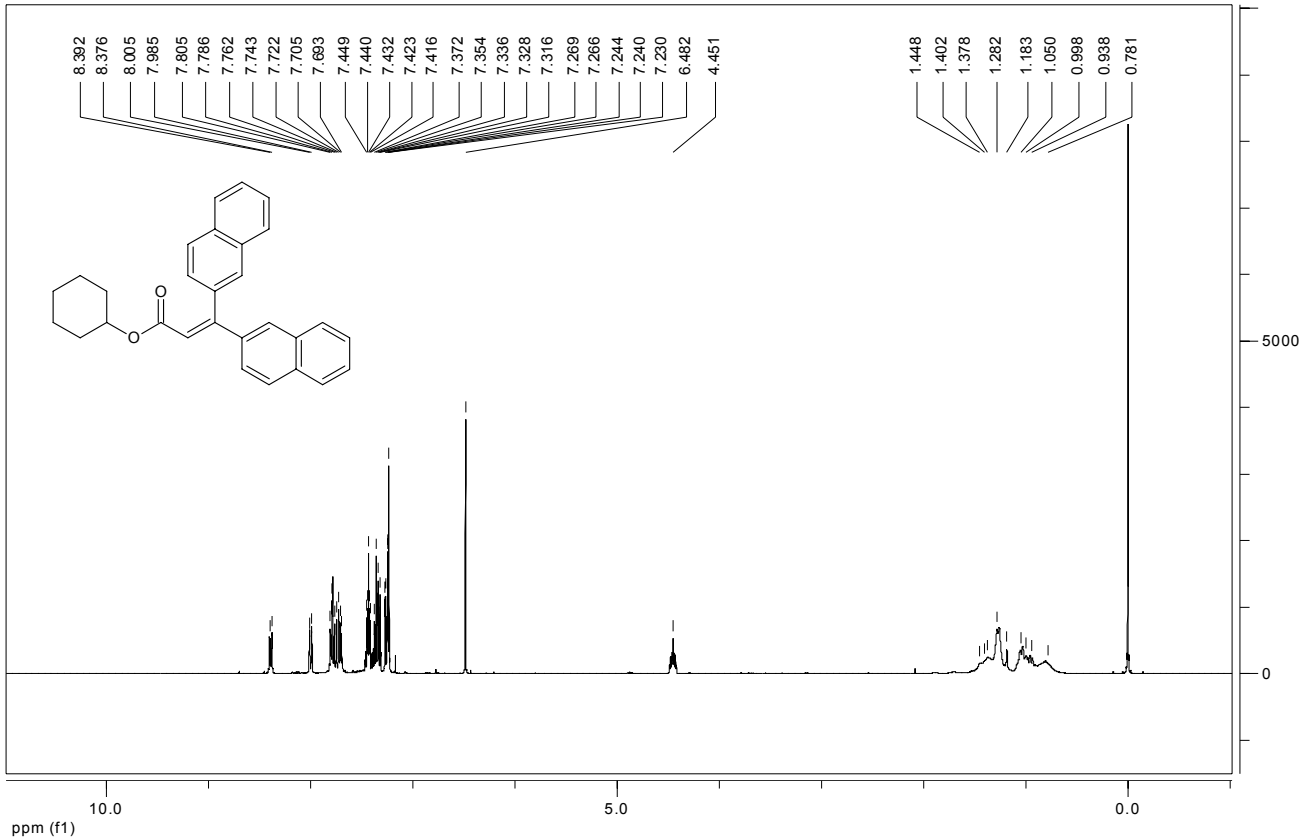


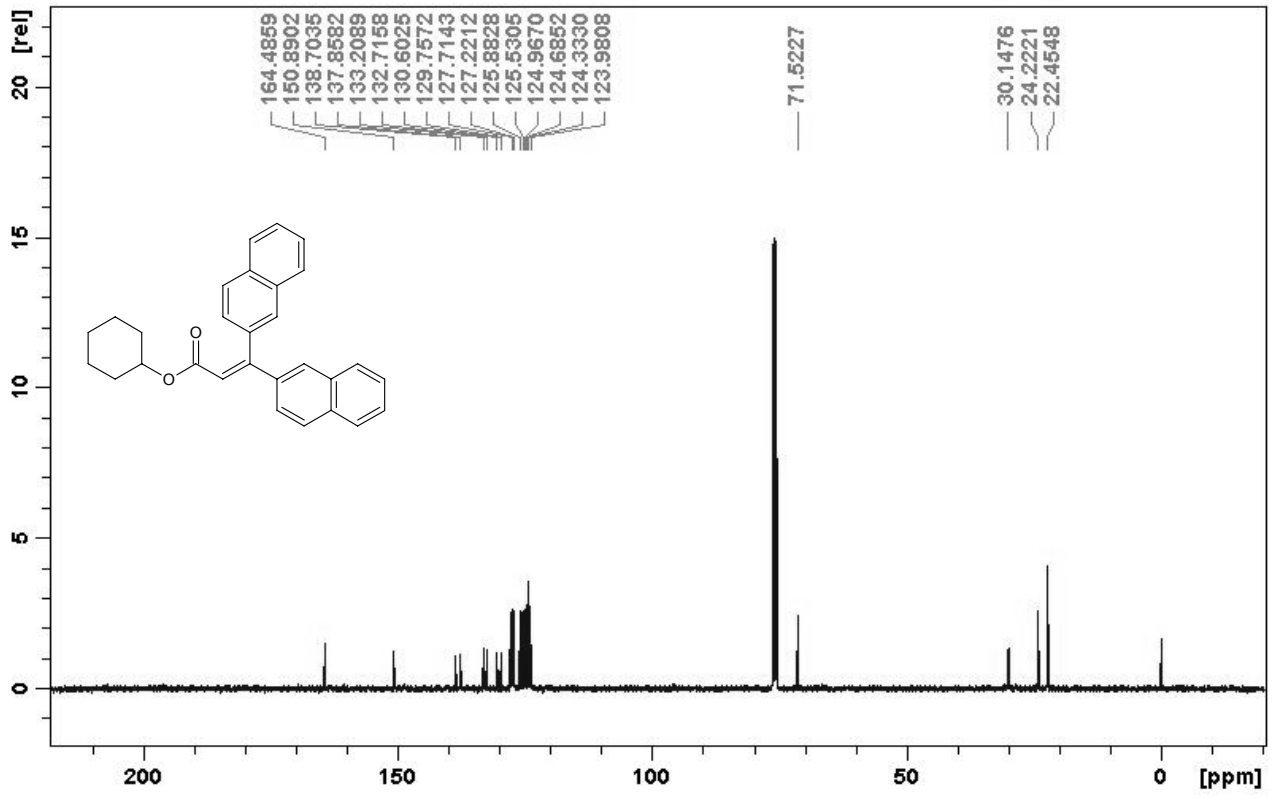
^{1}H NMR ($CDCl_3$, 400 MHz, mixture of cis and trans 50/50): 0.57 (t, *J*=8Hz, 3H, -CH_3), 0.76 (m, 3H), 1.01 (m, 2H), 1.17 (m, 4H), 1.41 (m, 2H), 3.68 (t, *J*=8Hz, 2H, -CH_2), 4.00 (t, *J*=8Hz, 2H, -CH_2), 6.10 (s, 1H, -CH=), 6.62 (s, 1H, -CH=), 7.18-7.85 (m, 24H, -CH=); ^{13}C NMR ($CDCl_3$, 400 MHz): 12.5, 17.8, 18.1, 29.2, 29.5, 63.0, 63.2, 118.6, 120.5, 124.0-128.4, 130.2, 130.6, 132.5, 132.9, 136.0, 138.5, 139.0, 153.2, 154.0, 165.0, 165.4; IR (cm^{-1}): 3057-2957-2871 (C-H), 1720 (C=O), 1614 (C=C), 1463, 1445, 1350, 1271, 1253, 1155 (C-O), 1061, 1018, 876, 798, 772, 736, 695; MS (EI): m/z =330 [M^+]**.**

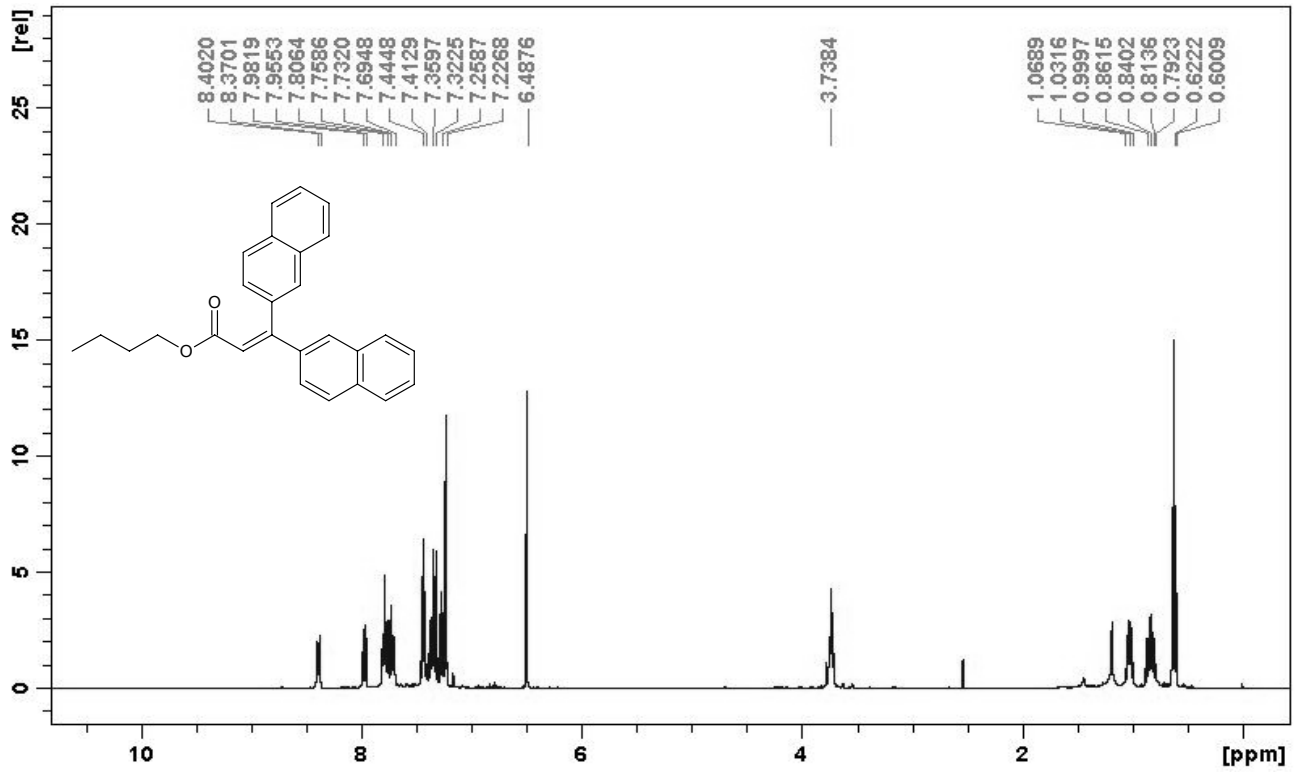

7.383
7.371
7.313
7.291
7.259
7.257
7.223
7.199
7.193
6.361
4.697
1.736
1.574
1.492
1.477
1.460
1.290
1.256
1.234
1.185
0.879
0.854
O
O
150
100
50
0
10.0
5.0
0.0
ppm (t1)

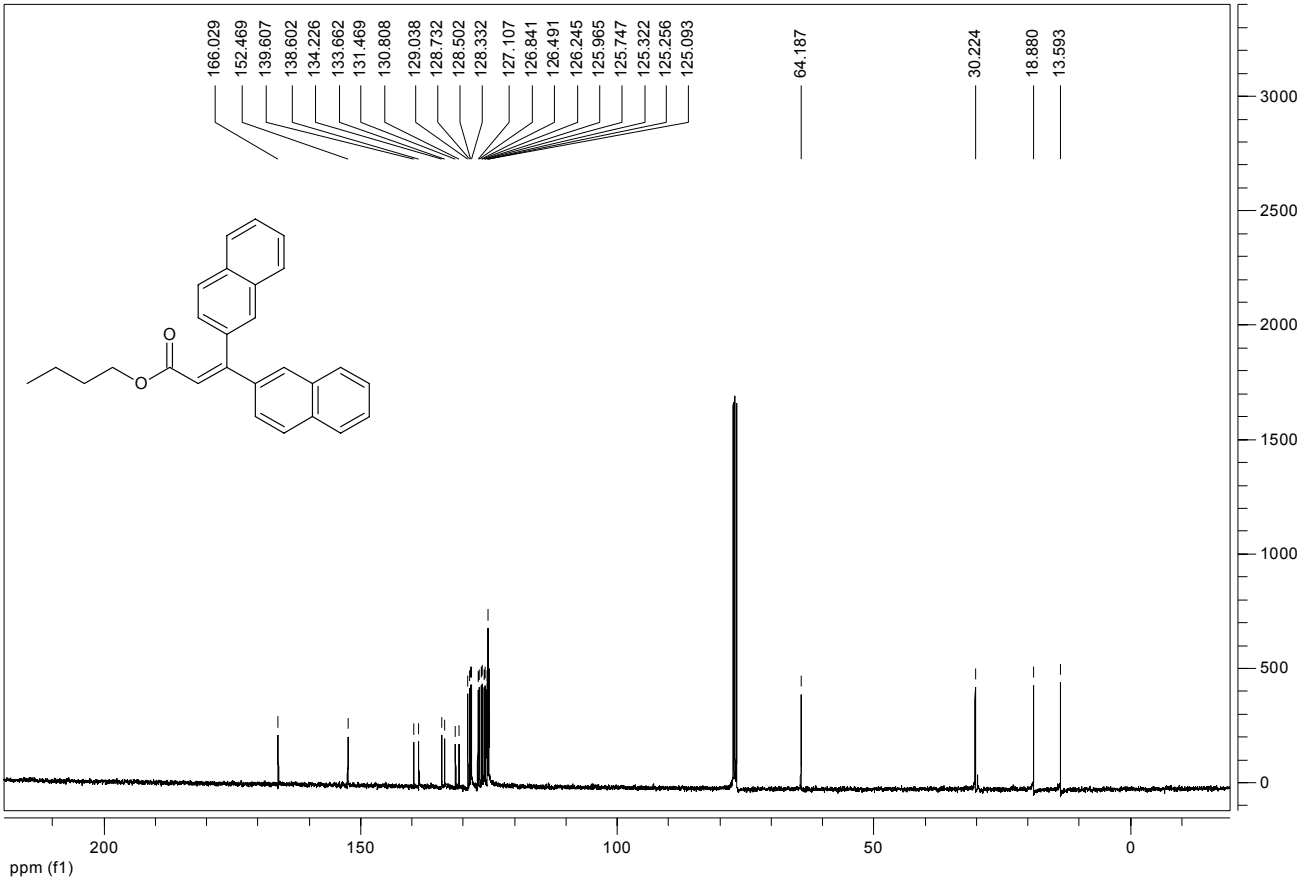

165.718
155.783
140.877
139.151
129.138
128.253
127.883
118.205
72.527
31.484
25.361
23.748
O
O
40000
30000
20000
10000
0
200
150
100
50
0
ppm (f1)

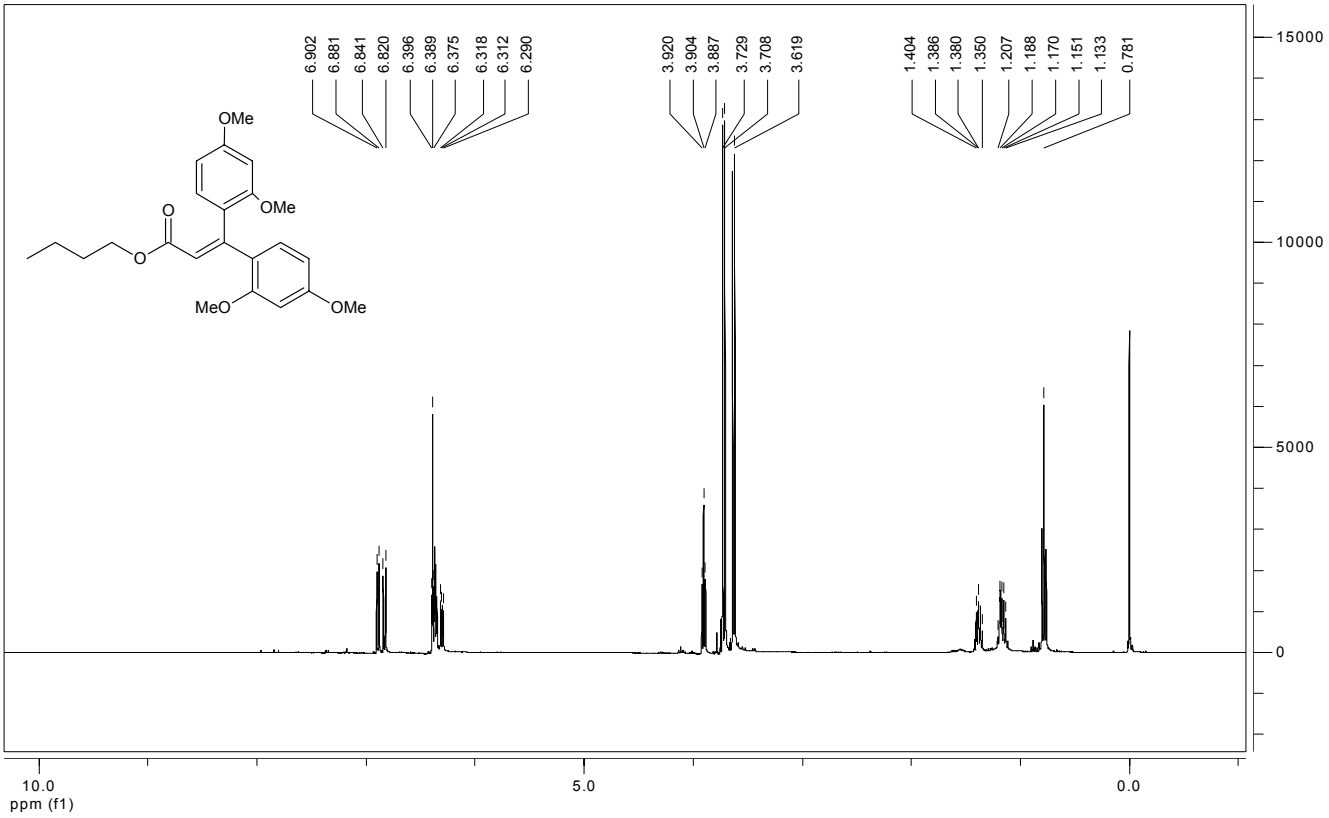

7.379
7.360
7.328
7.303
7.301
7.221
7.213
6.367
4.016
3.994
3.972
1.470
1.447
1.421
1.252
1.227
1.201
0.876
0.852
0.827
O
O
400
300
200
100
0
10.0
ppm (f1)
5.0
0.0

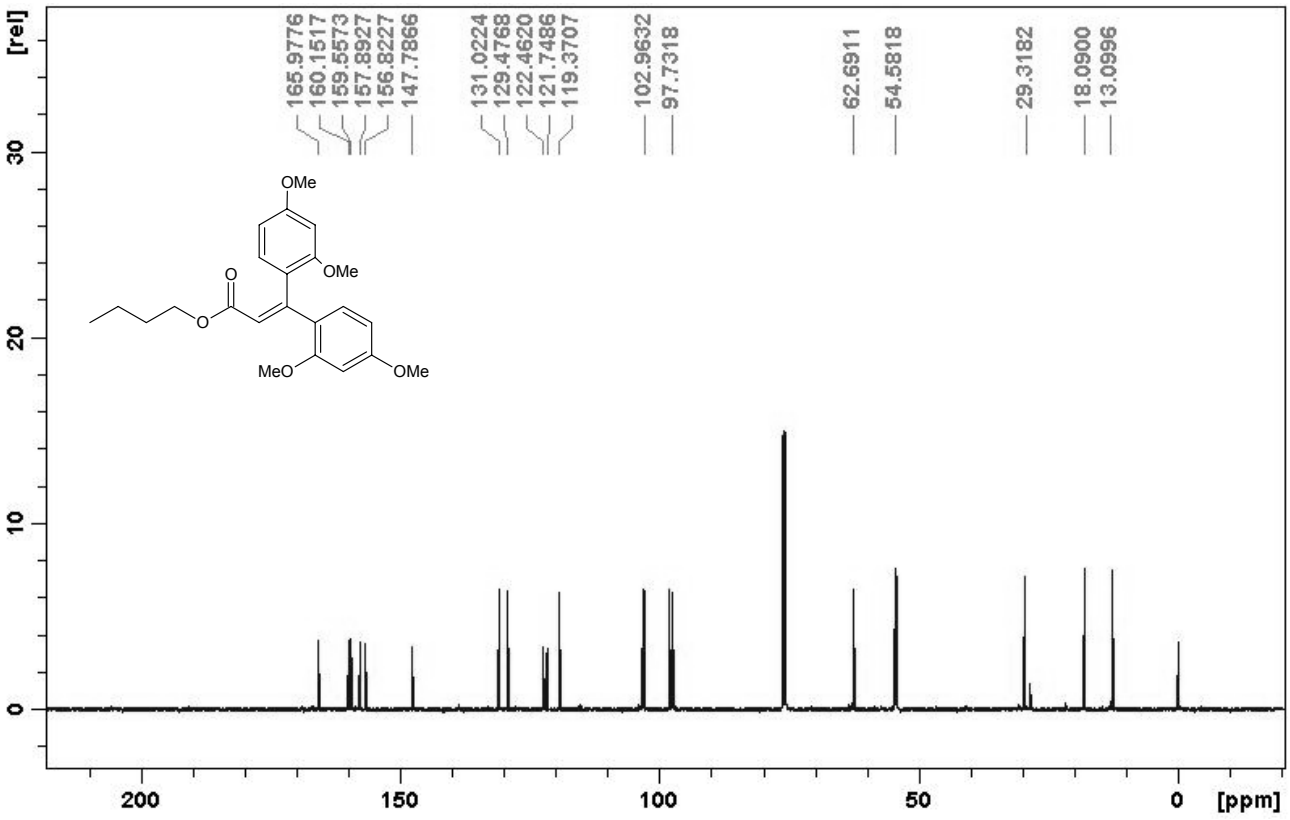

8.392
8.376
8.005
7.985
7.805
7.786
7.762
7.743
7.722
7.705
7.693
7.449
7.440
7.432
7.423
7.416
7.372
7.354
7.336
7.328
7.316
7.269
7.266
7.244
7.240
7.230
6.482
4.451
1.448
1.402
1.378
1.282
1.183
1.050
0.998
0.938
0.781
O
O
5000
0
10.0
5.0
0.0
ppm (f1)

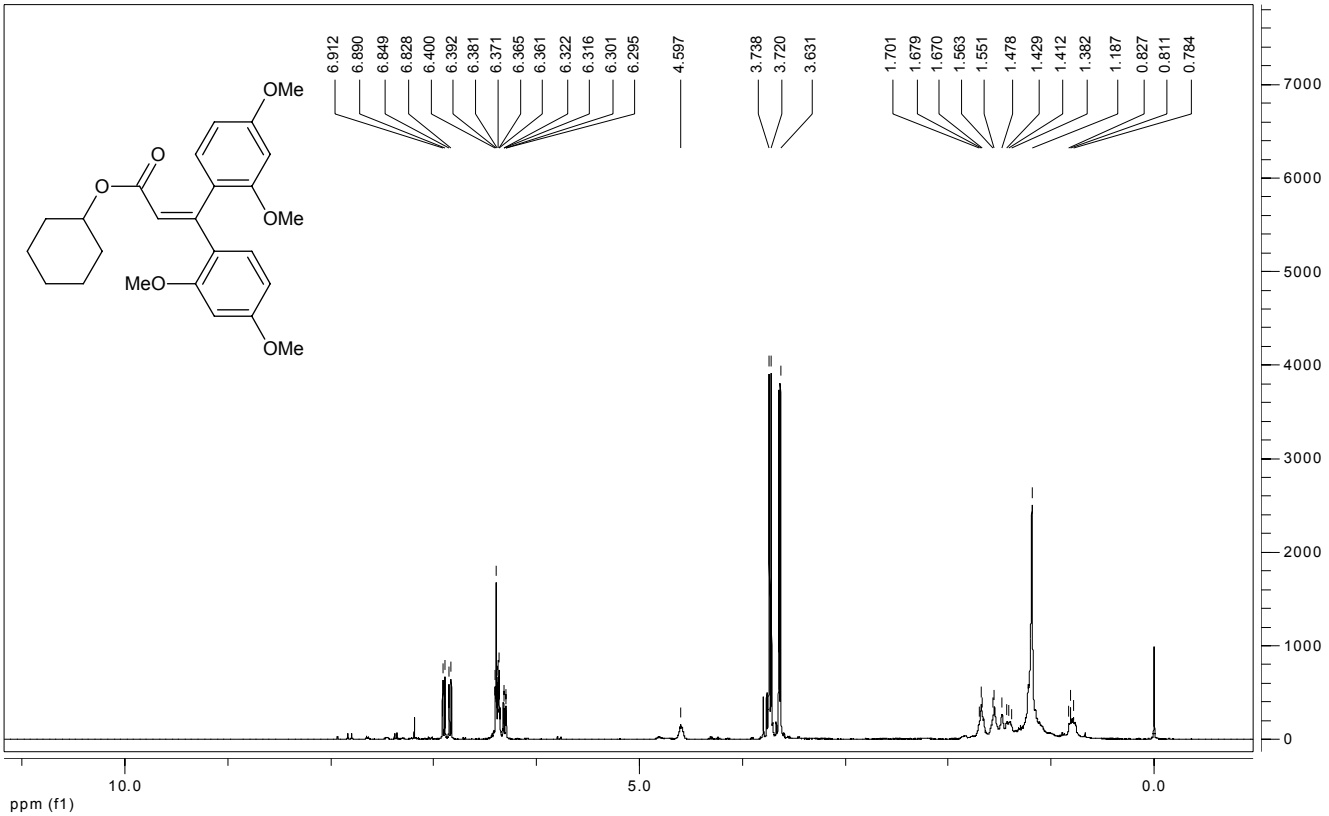

164.4859
150.8902
138.7035
137.8582
133.2089
132.7158
130.6025
129.7572
127.7143
127.2212
125.8828
125.5305
124.9670
124.6852
124.3330
123.9808
71.5227
30.1476
24.2221
22.4548
O
O
[rel]
20
15
10
5
0
200
150
100
50
0
[ppm]

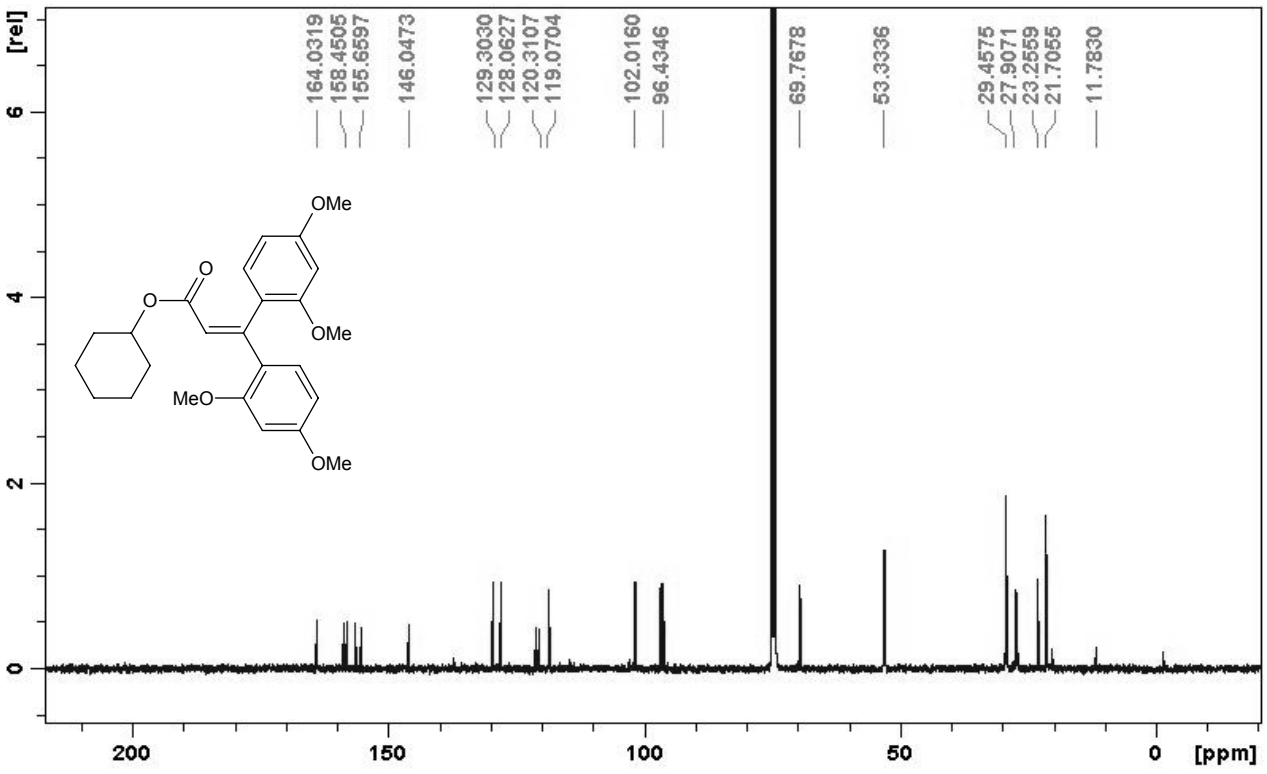

[rel]
8.4020
8.3701
7.9819
7.9553
7.8064
7.7586
7.7320
7.6948
7.4448
7.4129
7.3597
7.3225
7.2587
7.2268
6.4876
3.7384
1.0689
1.0316
0.9997
0.8615
0.8402
0.8136
0.7923
0.6222
0.6009
[ppm]

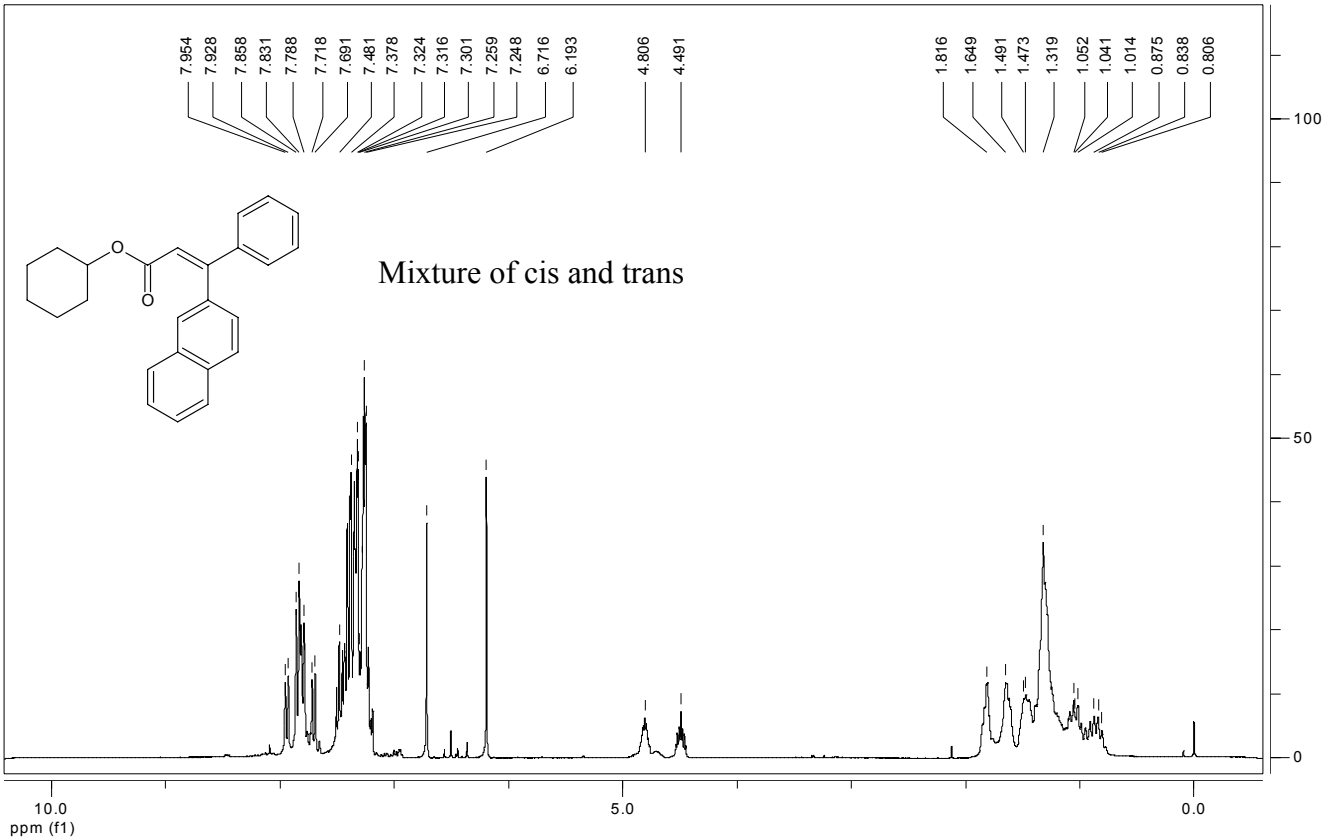

166.029
152.469
139.607
138.602
134.226
133.662
131.469
130.808
129.038
128.732
128.502
128.332
127.107
126.841
126.491
126.245
125.965
125.747
125.322
125.256
125.093
64.187
30.224
18.880
13.593
ppm (f1)

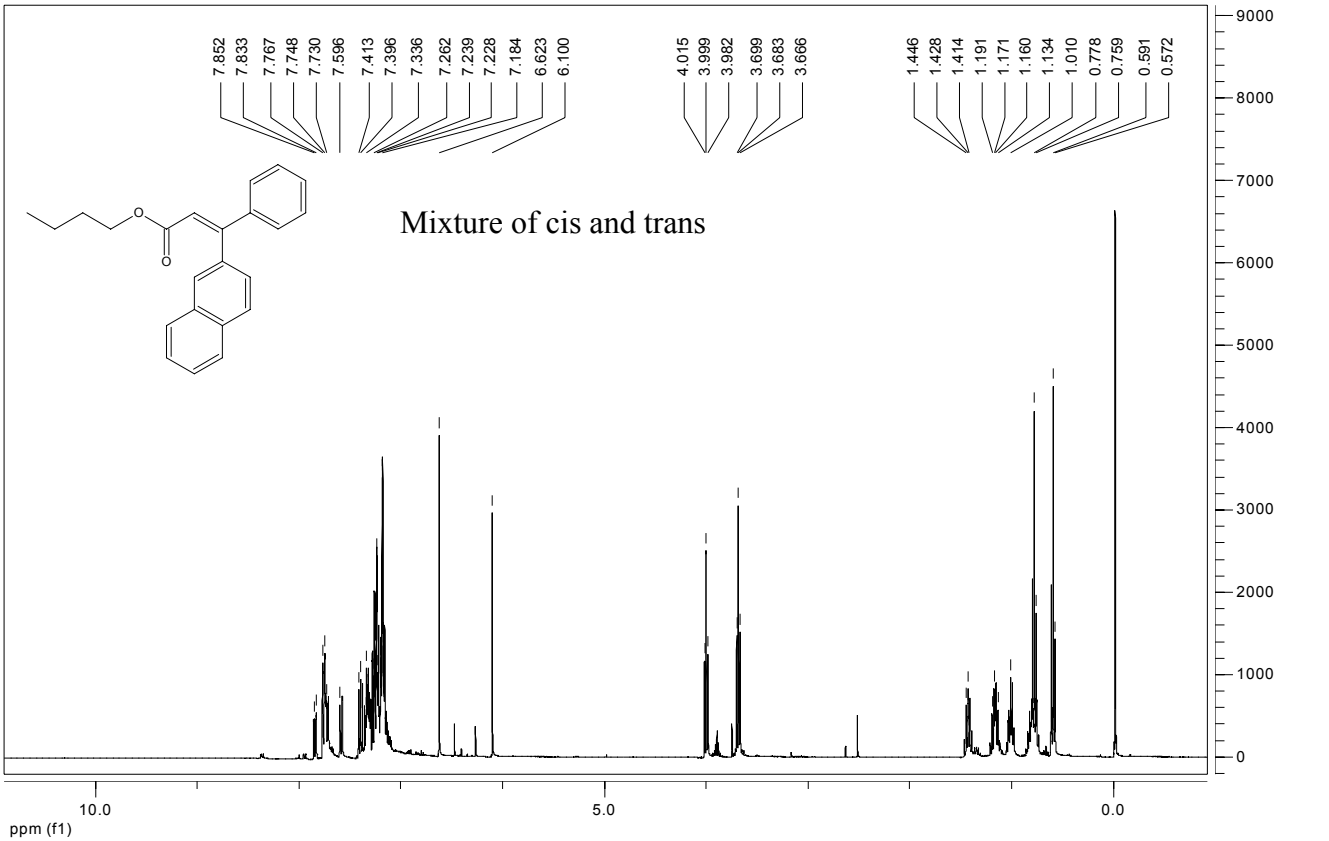

6.902
6.881
6.841
6.820
6.396
6.389
6.375
6.318
6.312
6.290
3.920
3.904
3.887
3.729
3.708
3.619
1.404
1.386
1.380
1.350
1.207
1.188
1.170
1.151
1.133
0.781
OMe
OMe
O
O
MeO
OMe
15000
10000
5000
0
10.0
ppm (f1)
5.0
0.0

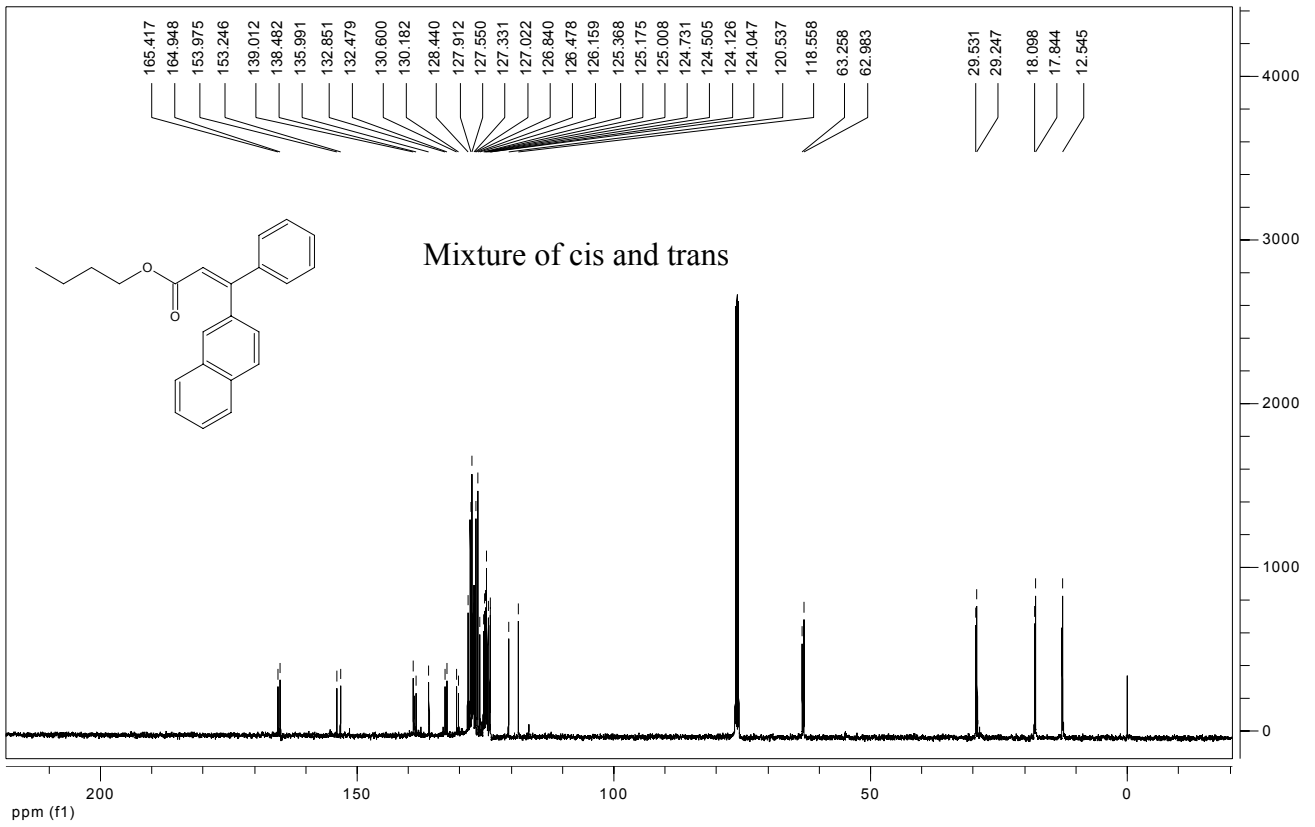

[rel]
165.9776
160.1517
159.5573
157.8927
156.8227
147.7866
131.0224
129.4768
122.4620
121.7486
119.3707
102.9632
97.7318
62.6911
54.5818
29.3182
18.0900
13.0996
OMe
OMe
O
O
MeO
OMe
30
20
10
0
200
150
100
50
0
[ppm]


6.912
6.890
6.849
6.828
6.400
6.392
6.381
6.371
6.365
6.361
6.322
6.316
6.301
6.295
4.597
3.738
3.720
3.631
1.701
1.679
1.670
1.563
1.551
1.478
1.429
1.412
1.382
1.187
0.827
0.811
0.784
OMe
O
O
OMe
MeO
OMe
7000
6000
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (f1)


[rel]
164.0319
158.4505
155.6597
146.0473
129.3030
128.0627
120.3107
119.0704
102.0160
96.4346
69.7678
53.3336
29.4575
27.9071
23.2559
21.7055
11.7830
OMe
O
O
OMe
MeO
OMe
6
4
2
0
200
150
100
50
0
[ppm]


7.954
7.928
7.858
7.831
7.788
7.718
7.691
7.481
7.378
7.324
7.316
7.301
7.259
7.248
6.716
6.193
4.806
4.491
1.816
1.649
1.491
1.473
1.319
1.052
1.041
1.014
0.875
0.838
0.806
Mixture of cis and trans
100
50
0
10.0
5.0
0.0
ppm (f1)


7.852
7.833
7.767
7.748
7.730
7.596
7.413
7.396
7.336
7.262
7.239
7.228
7.184
6.623
6.100
4.015
3.999
3.982
3.699
3.683
3.666
1.446
1.428
1.414
1.191
1.171
1.160
1.134
1.010
0.778
0.759
0.591
0.572
Mixture of cis and trans
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (f1)


165.417
164.948
153.975
153.246
139.012
138.482
135.991
132.851
132.479
130.600
130.182
128.440
127.912
127.550
127.331
127.022
126.840
126.478
126.159
125.368
125.175
125.008
124.731
124.505
124.126
124.047
120.537
118.558
63.258
62.983
29.531
29.247
18.098
17.844
12.545
Mixture of cis and trans
O
O
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)